

WHAT IS CLAIMED IS:

1. A process for the preparation of a hydrocyanation catalyst comprising an aqueous solution of at least one water-soluble phosphine and nickel values, which
5 comprises (a) admixing an aqueous solution of said at least one water-soluble phosphine with a nickel hydroxide, (b) adding hydrogen cyanide or a compound which generates hydrogen cyanide to the mixture thus formed, (c) stirring the resulting mixture until the nickel values have at least partially dissolved, and (d) reducing at least a portion of said nickel values having an oxidation state of
10 greater than zero to the zero oxidation state.
2. The process as defined by Claim 1, comprising maintaining stirring at a temperature of less than 100°C.
- 15 3. The process as defined by Claim 2, comprising maintaining stirring at a temperature ranging from 20°C to 80°C.
4. The process as defined by Claim 1, comprising adding nickel in the zero oxidation state to the mixture of reaction, prior to the reduction stage (d) thereof.
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5. The process as defined by Claim 1, comprising (b) adding hydrogen cyanide in an amount at least equal to the stoichiometric amount for converting nickel hydroxide into nickel cyanide.
- 25 6. The process as defined by Claim 5, comprising (b) adding a 30% to 200% stoichiometric excess of hydrogen cyanide.

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7. The process as defined by Claim 1, the amount of said at least one water-soluble phosphine, expressed as number of moles per 1 mol of nickel, ranging from 0.5 and 2,000.

5 8. The process as defined by Claim 7, said amount ranging from 2 to 300.

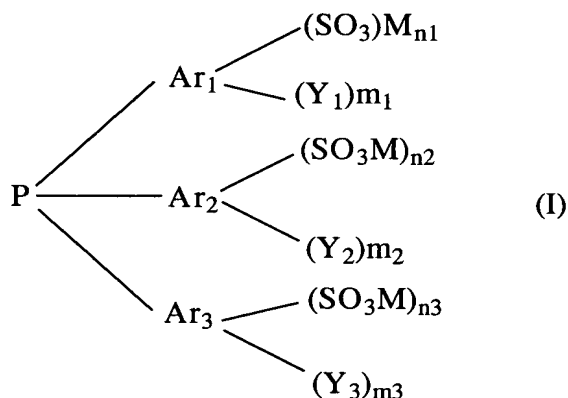
9. The process as defined by Claim 1, comprising (d) reducing said nickel values with gaseous hydrogen.

10 10. The process as defined by Claim 1, comprising (d) reducing said nickel values electrochemically.

11. The process as defined by Claim 1, comprising (d) reducing said nickel values with an organic/inorganic reducing agent.

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12. The process as defined by Claim 1, said at least one water-soluble phosphine having the structural formula (I):



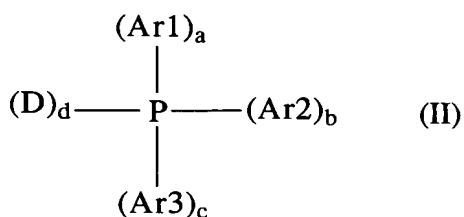
20 in which Ar₁, Ar₂ and Ar₃, which may be identical or different, are each an aryl radical; Y₁, Y₂ and Y₃, which may be identical or different, are each an alkyl

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radical having from 1 to 4 carbon atoms, an alkoxy radical having from 1 to 4 carbon atoms, a halogen atom, a CN group, an NO₂ group, an OH group, an NR₁R₂ radical, wherein R₁ and R₂, which may be identical or different, are each an alkyl radical having from 1 to 4 carbon atoms; M is an inorganic or organic cationic residue selected, such that the compound of formula (I) is soluble in water, from the group consisting of H⁺, cations derived from alkali metals or alkaline earth metals, N(R₃R₄R₅R₆)⁺, wherein R₃, R₄, R₅ and R₆, which may be identical or different, are each an alkyl radical having from 1 to 4 carbon atoms or a hydrogen atom, and other metal cations, the benzenesulfonic acid salts of which are soluble in water; m₁, m₂ and m₃ which may be identical or different, are each an integer ranging from 0 to 5; and n₁, n₂ and n₃, which may be identical or different, are each an integer ranging from 0 to 3, at least one of these being equal to or greater than 1.

13. The process as defined by Claim 12, said at least one water-soluble phosphine having the structural formula (I) comprising an alkali metal or alkaline earth metal salt, ammonium salt, or quaternary ammonium salt of (3-sulfo-4-methylphenyl)di(4-methylphenyl)phosphine, (3-sulfo-4-methoxyphenyl)di(4-methoxyphenyl)phosphine, (3-sulfo-4-chlorophenyl)di(4-chlorophenyl)phosphine, di(3-sulfophenyl)phenylphosphine, di(4-sulfophenyl)phenylphosphine, di(3-sulfo-4-methylphenyl)(4-methylphenyl)phosphine, di(3-sulfo-4-methoxyphenyl)(4-methoxyphenyl)phosphine, di(3-sulfo-4-chlorophenyl)(4-chlorophenyl)phosphine, tri(3-sulfophenyl)phosphine, tri(4-sulfophenyl)phosphine, tri(3-sulfo-4-methylphenyl)phosphine, tri(3-sulfo-4-methoxyphenyl)phosphine, tri(3-sulfo-4-chlorophenyl)phosphine, (2-sulfo-4-methylphenyl)(3-sulfo-4-methylphenyl)(3,5-disulfo-4-methylphenyl)phosphine or (3-sulfophenyl)(3-sulfo-4-chlorophenyl)(3,5-disulfo-4-chlorophenyl)phosphine.

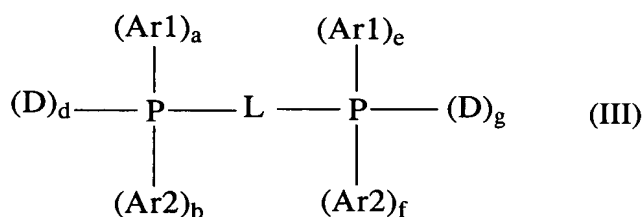
14. The process as defined by Claim 1, said at least one water-soluble phosphine having the structural formula (II):



5 in which Ar1 and Ar2, which may be identical or different, are each aryl radicals or substituted such aryl radicals bearing one or more of the following substituents: alkyl or alkoxy radicals having from 1 to 4 carbon atoms, halogen atoms, the hydrophilic groups -COOM, -SO₃M or -PO₃M, wherein M is an inorganic or organic cationic residue selected from among hydrogen, cations derived from alkali metals or alkaline earth metals, ammonium cations -N(R)₄, wherein the radicals R, which may be identical or different, are each a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, and other cations derived from metals, the arylcarboxylic acid, arylsulfonic acid or arylphosphonic acid salts of which are soluble in water, -N(R)₄, wherein the radicals R, which may be identical or different, are each a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, or -OH; Ar₃ is a substituted aryl radical bearing one or more of the following substituents: alkyl or alkoxy radicals having from 1 to 4 carbon atoms, halogen atoms, the hydrophilic groups -COOM or -PO₃M, wherein M is an inorganic or organic cationic residue selected from among hydrogen, cations derived from alkali metals or alkaline earth metals, ammonium cations -N(R)₄, wherein the radicals R, which may be identical or different, are each a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, and other metal cations, the arylcarboxylic acid or arylphosphonic acid salts of which are soluble in water, N(R)₄, wherein the radicals R, which may be identical or different, are each a

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hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, or -OH, with the proviso that at least one of the substituents of Ar₃ is a hydrophilic group as defined above; a is 0 or 1; b is 0 or 1; c is an integer ranging from 0 to 3; D is an alkyl radical, a cycloalkyl radical or an alkyl or cycloalkyl radical substituted by one or more of the following substituents: an alkoxy radical having from 1 to 4 carbon atoms, a halogen atom, a hydrophilic group -COOM, -SO₃M or -PO₃M, wherein M is an inorganic or organic cationic residue selected from among hydrogen, cations derived from alkali metals or alkaline earth metals, ammonium cations -N(R)₄, wherein the radicals R, which may be identical or different, are each a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, and other metal cations, the arylcarboxylic acid, arylsulfonic acid or arylphosphonic acid salts of which are soluble in water, -N(R)₄, wherein the radicals R, which may be identical or different, are each a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, -OH; d is an integer ranging from 0 to 3; and the sum (a+b+c+d) is equal to 3 or having the structural formula (III):



in which Ar1, Ar2 and D are as defined above for the formula (II); a, b, e, and f are each 0 or 1; d and g are each an integer ranging from 0 to 2; the sum (a+b+d) is equal to 2; the sum (e+f+g) is equal to 2; and L is a single valency bond or a divalent hydrocarbonaceous radical, or a radical deriving from a heterocycle comprising one or two oxygen, nitrogen or sulfur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or both phosphorus atoms or being bonded to one of the phosphorus atoms or to

both via a linear or branched alkylene radical having from 1 to 4 carbon atoms, with the proviso that the ring or rings which are optionally moieties of the divalent radical L optionally bear one or more substituents.

- 5 15. The process as defined by Claim 14, said at least one water-soluble phosphine having the structural formula (II) or (III) comprising tris(hydroxymethyl)phosphine, tris(2-hydroxyethyl)phosphine, tris(3-hydroxypropyl)phosphine, tris(2-carboxymethyl)phosphine, the sodium salt of tris(3-carboxyphenyl)phosphine, tris(3-carboxyethyl)phosphine, tris(4-trimethylammonio-10 phenyl)phosphine iodide, the sodium salt of tris(2-phosphonoethyl)phosphine, bis(2-carboxyethyl)phenylphosphine, the sodium salt of 2,2'-bis[di(sulfophenyl)phosphino]-1,1'-binaphthyl, the sodium salt of 1,2-bis[di(sulfophenyl)phosphinomethyl]cyclobutane (CBDTS), 1,2-bis(dihydroxymethylphosphino)ethane, 1,3-15 bis(dihydroxymethylphosphino)propane, or the sodium salt of 2,2'-bis[di(sulfophenyl)phosphinomethyl]-1,1'-binaphthyl.

- 20 16. The hydrocyanation catalyst comprising an aqueous solution of at least one water-soluble phosphine and nickel values, prepared by the process which comprises (a) admixing an aqueous solution of said at least one water-soluble phosphine with a nickel hydroxide, (b) adding hydrogen cyanide or a compound which generates hydrogen cyanide to the mixture thus formed, (c) stirring the resulting mixture until the nickel values have at least partially dissolved, and (d) 25 reducing at least a portion of said nickel values having an oxidation state of greater than zero to the zero oxidation state.

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